

# Cold Collision Frequency Shift of an Optical Spectrum of a Trapped Gas

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We develop an exact sum rule that relates the spectral shift of a trapped gas undergoing cold collisions to measurable quantities of the system. The method demonstrates the dependence of the cold collision frequency shift on the quantum degeneracy of the gas and facilitates extracting scattering lengths from the data. We apply the method to analyzing spectral data for magnetically trapped hydrogen atoms and determine the value of the  $1S - 2S$  scattering length.

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The broadening and shifting of spectral lines of a gas by collisions was among the earliest discoveries in the development of high precision spectroscopy [1]. The pressure shift, which originates in interatomic perturbations [2], is particularly simple to interpret at low temperatures where the thermal de Broglie wavelength  $\Lambda_T = h/(2\pi mk_B T)^{1/2}$  is much larger than the scattering length  $a$  [3] and the interactions arise only through  $s$ -wave scattering. In this *cold collision* regime, the frequency shift is much larger than the level broadening.

The theory of the cold collision shift has been developed to interpret hyperfine transitions in cryogenic hydrogen masers and laser cooled atomic fountains [4]. In this work we study the shift for optical excitation in a system that can be quantum degenerate, and apply the results to data on  $1S - 2S$  two-photon excitation of trapped atomic hydrogen [5].

For the case of a homogeneous sample of density  $n$ , and a coherent, weak excitation that couples two inner states of the atoms, we find

$$\hbar\Delta\omega_{\text{coll}} = g_2(\lambda_{12} - \lambda_{11})n, \quad \lambda_{\alpha\beta} = 4\pi\hbar^2 a_{\alpha\beta}/m. \quad (1)$$

Here  $g_2$  is the equal point value of the second order correlation function [6],  $g_2 \equiv g^{(2)}(\vec{r} = 0)$ , the state 1(2) is the ground(excited) state, and  $a_{\alpha\beta}$  is the  $s$ -wave scattering length for  $\alpha - \beta$  collisions.

Equation (1) shows that quantum correlations in the system are manifest in the collision shift. For a uniform Bose gas in thermal equilibrium  $g_2 = 2 - (n_{\text{BEC}}/n)^2$  [7], where  $n_{\text{BEC}}$  is the density of condensed atoms. Above the condensation temperature, when  $n_{\text{BEC}} = 0$ ,  $g_2$  equals 2, in which case Eq.(1) is in agreement with previous work [4]. At zero temperature, for a pure condensate with  $n_{\text{BEC}} = n$ , the collision shift is half of the shift for a non-condensed gas. Equation (1) generalizes the result [4] to  $T < T_{\text{BEC}}$  and relates the spectral shift to the condensate fraction.

It is quite remarkable that the factor  $g_2$  in Eq.(1) multiplies *both*  $\lambda_{12}$  and  $\lambda_{11}$ . This results from correlations between an excited atom and other atoms. During the excitation, the internal states of the atoms are rotated:  $\cos\theta(t)|1S\rangle + e^{-i\phi(t)}\sin\theta(t)|2S\rangle$ . The angles  $\theta(t)$ ,  $\phi(t)$  depend on laser power and on the atom's trajectory in

the laser field, specific for each atom. However, for small excitation power, the angle  $\theta(t)$  is small, and thus the internal states of all atoms remain nearly identical while the laser is on, even if the excitation field is spatially nonuniform. Therefore, during the excitation the atoms interact as identical particles. This causes the short range statistical correlations in the initial state to be replicated in the excited state of the gas, which results in the statistical factor  $g_2$  in the first term of Eq.(1).

The transfer of spatial correlations to the excited state is not limited to weak excitation. For the case of strong excitation, spatial correlations in the ground state will also be transferred to the excited state, but only provided the excitation scheme is coherent. The difference between coherent and incoherent cases can be seen from comparing two examples, the coherent superposition of the ground and excited states obtained, e.g., by a  $\pi/2$  pulse, and the incoherent mixture state resulting from saturating the Rabi transition. These states will both have equal populations in the two internal states, but quite different correlations. In the former case of a pure internal state the spatial correlation will be the same as for the ground state of indistinguishable particles. In the latter case of a mixed state the correlations will be reduced. Consequently, the correlation energy of the first state will exceed that of the second state by the factor  $g_2$ .

To emphasize the non-trivial character of the result Eq.(1), let us point out that  $\hbar\Delta\omega_{\text{coll}}$  differs from the thermodynamic work needed to transfer one atom from the state 1 to the state 2. The latter work, calculated by removing one atom from the sample, and then introducing an atom in state 2 from far away, ignoring entropy, is given by  $(\lambda_{12} - g_2\lambda_{11})n$ . Here  $\lambda_{12}n$  is the energy of interaction of the excited atom with the atoms in the state 1, and  $g_2\lambda_{11}n$  is the chemical potential of a Bose gas. The key difference between this process and optical excitation, resulting in the different dependence on  $g_2$ , is the incoherence of the state of the added atom with the initial state of the sample.

To calculate the full optical spectrum shape of a trapped gas in the cold collision regime, other factors would have to be considered in addition to the effects

of statistical correlations. Optical coherence can be lost via dephasing elastic collisions, giving rise to collisional broadening. One would have also to take into account atomic motion in the trap and the effects of the inhomogeneous density distribution in the sample, especially in the Bose-Einstein condensate. In addition, the interaction may give rise to a doublet structure of the spectrum [9]. Altogether, these effects can lead to a complicated broadened spectrum with asymmetric lines [5,10,11]. However, we demonstrate below that the spectrum's center of mass obeys a simple and exact sum rule and is insensitive to these additional effects.

We lay out the theory of the shift by deriving a sum rule (Eq.(12)) that relates the center of mass of the observed spectrum to measurable experimental parameters. The sum rule bridges between the uniform density result Eq.(1) and experimentally measured spectra. The sum rule accounts for all interactions between atoms occurring in the  $s$ -wave scattering channel, which includes the  $s$ -wave collisional broadening. It follows from the sum rule that collisional broadening as well as the time of flight broadening resulting from atomic motion in the trap do not contribute to the spectral shift. At the same time, the effects on the shift of inhomogeneity in the gas density and non-uniformity in the excitation field are expressed in the sum rule Eq.(12) in an exact and straightforward way.

We start by considering a homogeneous Bose gas and derive Eq.(1). Then for the realistic situation of a trapped gas sample we derive the sum rule Eq.(12), a generalization of Eq.(1). The sum rule is exact and general, applicable both to Doppler-free and Doppler-sensitive spectra. Finally we apply the sum rule to experimental data on the spectrum of cold trapped hydrogen to calculate the  $1S - 2S$  scattering length for hydrogen. **The system:** To provide the context for the theory, we briefly describe the experimental situation. The temperature of the hydrogen is  $30 - 100 \mu\text{K}$ , well below the cold collision threshold  $T \simeq 1 \text{ K}$  [3]. The atoms are spin polarized and interact in the triplet channel. Calculated values of the  $1S - 1S$  and  $1S - 2S$  triplet scattering lengths are  $a_{11} = 0.0648 \text{ nm}$  [14] and  $a_{12} = -2.3 \text{ nm}$  [18]. We neglect  $2S - 2S$  scattering because the excitation rate is assumed low (in the experiment typically  $10^{-4}$  of the atoms are excited) so the background gas is essentially pure  $1S$ . Since  $|a_{12}| \gg a_{11}$ , collisions between  $1S$  and  $2S$  atoms dominate the shift, which is to the red.

Each atom will be in some superposition of the ground state  $1S$  and the excited state  $2S$ . In the second quantization formalism, the atoms are described by the canonical Bose operators  $\psi_1(r)$  and  $\psi_2(r)$ . The Hamiltonian is  $\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_{\text{int}}$ , where  $\mathcal{H}_0$  describes atoms freely moving in the trap, and  $\mathcal{H}_{\text{int}}$  is the interaction term:

$$\mathcal{H}_0 = \int \sum_{\alpha=1,2} \psi_{\alpha}^{\dagger}(r) \left( -\frac{\hbar^2 \nabla^2}{2m} + U(r) \right) \psi_{\alpha}(r) d^3r, \quad (2)$$

$$\mathcal{H}_{\text{int}} = \frac{1}{2} \int \sum_{\alpha,\beta=1,2} \lambda_{\alpha\beta} \psi_{\alpha}^{\dagger}(r) \psi_{\beta}^{\dagger}(r) \psi_{\beta}(r) \psi_{\alpha}(r) d^3r. \quad (3)$$

Here  $U(r)$  is the trap potential (essentially the same for the  $1S$  and the  $2S$  states).

Inelastic collisions, such as collisions in which the hyperfine level of one or both of the colliding partners changes, may contribute additional shifts which are not accounted for in this formalism. However, these effects, as well as the three-body collision effects, are small in the experiment and can be neglected.

The two-photon  $1S - 2S$  spectrum consists of Doppler-free and Doppler-sensitive excitations. In the Doppler-free situation, the transition results from absorbing two counter-propagating photons with equal frequencies and zero net momentum. In the absence of interactions, the resonance condition is  $2\omega_{\text{laser}} = \omega_0$ , where  $\omega_0$  corresponds to the resonance of a single free atom. In the Doppler-sensitive situation, the transition is caused by two photons propagating in the same direction. For a free atom, the resonance frequency is shifted by the recoil energy:  $2\hbar\omega_{\text{laser}} = \hbar\omega_0 + (2k)^2/2m$ , where  $k = \hbar\omega/c$  is photon momentum and  $m$  is the atom mass.

Radiative excitation in a many particle system is described by adding to the Hamiltonian (2),(3) the term

$$\mathcal{H}_{\text{rad}} = \int d^3r \left( A(r) e^{-i\omega t} \psi_2^{\dagger}(r) \psi_1(r) + \text{h.c.} \right), \quad (4)$$

where  $\omega = 2\omega_{\text{laser}} - \omega_0$ . The two-photon excitation field  $A(r)$  is equal, up to a constant factor, to the square of the electric field. Spatial variation of  $A(r)$  in the Doppler-free case occurs on a scale set by the focused laser beam diameter, and in the Doppler-sensitive case is given by  $\tilde{A}(r) \cos(2kr + \phi(r))$ , where  $\tilde{A}(r)$  and  $\phi(r)$  are slowly varying functions.

**A tutorial example:** Before discussing the general case, here we derive the mean frequency shift for the Doppler-free transition caused by a uniform excitation field  $A(r) = A_0$ , ignoring the  $1S - 1S$  interactions ( $\lambda_{11} = 0$ ). To that end, consider a gas of  $N$  atoms confined in a box of volume  $V$ . Since we ignore the  $1S - 1S$  interaction, the many body state ground state of the system  $\Phi_0$  is simply a symmetrized product of single particle states. It can be characterized by occupation numbers  $n_j$  of the single particle plane wave states  $V^{-1/2} e^{ik_j r}$ ,  $\sum_j n_j = N$ . Initially, the internal state of all atoms is  $1S$ .

The excited state, to lowest order in the excitation, is given by  $\Phi_1 = \mathcal{H}_{\text{rad}} \Phi_0$ . We consider the norm  $\|\Phi_1\|^2$  and the expectation value of the interaction  $\langle \Phi_1 | \mathcal{H}_{\text{int}} | \Phi_1 \rangle$ . The ratio of these quantities gives the mean frequency shift. Because  $\Phi_0$  is the product of plane wave states in a box, the frequency shift can be evaluated exactly.

The norm  $\langle \Phi_1 | \Phi_1 \rangle$  of the excited state is given by

$$\|\Phi_1\|^2 = |A_0|^2 \int \langle \Phi_0 | \psi_1^\dagger(r) \psi_2(r) \psi_2^\dagger(r') \psi_1(r') | \Phi_0 \rangle d^3r d^3r' . \quad (5)$$

To evaluate the norm one first puts the operators  $\psi_2(r)$  and  $\psi_2^\dagger(r')$  in (5) in normal order by using the commutation relation  $[\psi_2(r), \psi_2^\dagger(r')] = \delta(r - r')$ . Noting that  $\psi_2(r)|\Phi_0\rangle = 0$ , the norm is given by

$$\|\Phi_1\|^2 = |A_0|^2 \int \langle \Phi_0 | \psi_1^\dagger(r) \psi_1(r) | \Phi_0 \rangle d^3r = |A_0|^2 N . \quad (6)$$

To obtain the frequency shift  $\Delta\omega_{\text{coll}}$ , we consider the expectation value  $\langle \Phi_1 | \mathcal{H}_{\text{int}} | \Phi_1 \rangle$ , keeping in  $\mathcal{H}_{\text{int}}$  only the  $1S - 2S$  interaction  $\lambda_{12}$ . After arranging in normal order, as in the calculation of the norm  $\|\Phi_1\|^2$ , one has

$$\langle \Phi_1 | \mathcal{H}_{\text{int}} | \Phi_1 \rangle = \lambda_{12} |A_0|^2 \int \langle \Phi_0 | \psi_1^\dagger(r) \psi_1^\dagger(r) \psi_1(r) \psi_1(r) | \Phi_0 \rangle d^3r . \quad (7)$$

Evaluating the expectation value for  $\Phi_0$  chosen as a product of plane wave states, one expresses Eq.(7) in terms of the occupation numbers of the ground and excited states as

$$\langle \Phi_1 | \mathcal{H}_{\text{int}} | \Phi_1 \rangle = \lambda_{12} \frac{|A_0|^2}{V} \left( 2 \sum_{i \neq j} n_i n_j + \sum_i n_i (n_i - 1) \right) . \quad (8)$$

The mean frequency shift is then given by the ratio of (8) and the norm (6):

$$\hbar \Delta\omega_{\text{coll}} = \frac{\lambda_{12}}{VN} \left( 2N^2 - \sum_i n_i (n_i + 1) \right) . \quad (9)$$

The formal reason for the factor 2 to appear in Eqs. (8, 9) and, eventually for  $g_2$  to appear in Eq.(1), is the following. In taking the average in Eq.(7) by Wick's theorem [13], there are two essentially different ways to pair the operators, analogous to the Hartree and Fock contributions to the energy. For short range interaction between bosons, the Hartree and Fock contributions are equal and as a result the frequency shift is twice as large as the “mean density” result.

In the thermodynamic limit,  $V, N \rightarrow \infty$ ,  $n = N/V$  constant, the second term in Eq.(9) contributes only when there are states filled by a macroscopic number of particles. For example, in thermodynamic equilibrium at  $T < T_{\text{BEC}}$ , the shift Eq.(9) is  $\lambda_{12}(2n - n_c^2/n)$ , whereas in a non degenerate gas, at  $T > T_{\text{BEC}}$ , the shift is  $2\lambda_{12}n$ .

**The sum rule:** We turn now to deriving a sum rule that generalizes the result Eq.(1) to non-homogeneous samples and spatially varying excitation field (and  $\lambda_{11} \neq 0$ ).

We start with the Golden Rule formula for the absorption spectrum,

$$\mathcal{I}(\omega) = \frac{2\pi}{\hbar} \sum_{E_i, E_f} \delta(\hbar\omega + E_i - E_f) |\langle f | \mathcal{H}_{\text{rad}} | i \rangle|^2 p_i , \quad (10)$$

where  $|i\rangle$ ,  $|f\rangle$  are eigenstates of the Hamiltonian  $\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_{\text{int}}$  with the energies  $E_i$ ,  $E_f$ , and  $p_i$  is the statistical occupation of the states  $|i\rangle$ .

The sum rule for the spectrum  $\mathcal{I}(\omega)$  is found by evaluating the first moment:

$$\begin{aligned} \int \omega \mathcal{I}(\omega) \frac{d\omega}{2\pi} &= \frac{1}{\hbar^3} \sum_{E_i, E_f} (E_f - E_i) |\langle f | \mathcal{H}_{\text{rad}} | i \rangle|^2 p_i \\ &= \frac{1}{\hbar^3} \sum_{E_i, E_f} \langle i | \mathcal{H}_{\text{rad}} | f \rangle \langle f | [\mathcal{H}, \mathcal{H}_{\text{rad}}] | i \rangle p_i \\ &= \frac{1}{\hbar^3} \sum_{E_i} \langle i | \mathcal{H}_{\text{rad}} [\mathcal{H}, \mathcal{H}_{\text{rad}}] | i \rangle p_i . \end{aligned} \quad (11)$$

In obtaining this result we first integrated the delta function, then wrote the result as a matrix element of the commutator  $[\mathcal{H}, \mathcal{H}_{\text{rad}}]$  and, finally, used the completeness relation.

Now we consider contributions of the different terms of the Hamiltonian to the sum rule. The potential energy operator  $\int (\psi_1^\dagger \psi_1 + \psi_2^\dagger \psi_2) U(r) d^3r$  commutes with  $\mathcal{H}_{\text{rad}}$ , and thus does not contribute. There are two contributions, first from the interaction Hamiltonian, second from the kinetic energy operator, denoted by  $F_{\text{int}}$  and  $F_{\text{kin}}$  respectively. The sum rule becomes

$$\int \omega \mathcal{I}(\omega) \frac{d\omega}{2\pi} = F_{\text{int}} + F_{\text{kin}} . \quad (12)$$

For Doppler-free excitation  $F_{\text{kin}}$  is small compared to  $F_{\text{int}}$ , whereas for Doppler-sensitive excitation it contributes the larger shift.

First, consider the interaction  $\mathcal{H}_{\text{int}}$ , and calculate  $F_{\text{int}}$ . After evaluating the commutator in Eq.(11), one follows the same procedure as in the above calculation of the norm  $\|\Phi_1\|$ . The result is

$$F_{\text{int}} = \left\langle \int (\lambda_{12} - \lambda_{11}) |A(r)|^2 \psi_1^\dagger(r) \psi_1^\dagger(r) \psi_1(r) \psi_1(r) \frac{d^3r}{\hbar^3} \right\rangle , \quad (13)$$

where  $\langle \dots \rangle$  means  $\sum_{E_i} \langle i | \dots | i \rangle p_i$ . The expectation value  $\langle : (\psi_1^\dagger(r) \psi_1(r))^2 : \rangle = G_2(r)$ , the two-particle density. (Here  $: \dots :$  indicates canonical normal ordering.) Finally, using the statistical factor  $g_2 = G_2/n^2$ , the result is

$$F_{\text{int}} = \int (\lambda_{12} - \lambda_{11}) |A(r)|^2 g_2 n^2(r) \frac{d^3r}{\hbar^3} . \quad (14)$$

Next, we calculate  $F_{\text{kin}}$ , the contribution to the sum rule coming from the kinetic energy operator

$-(\hbar^2/2m) \int (\psi_1^\dagger \nabla^2 \psi_1 + \psi_2^\dagger \nabla^2 \psi_2) d^3r$ . After evaluating the commutator with  $\mathcal{H}_{\text{rad}}$ , one has

$$F_{\text{kin}} = -\frac{\hbar^2}{2m} \left\langle \int \psi_1^\dagger(r) A^*(r) [\nabla^2, A(r)] \psi_1(r) \frac{d^3r}{\hbar^3} \right\rangle. \quad (15)$$

Integrating by parts, and writing the excitation field as  $A(r) = |A(r)|e^{i\theta}$ , yields

$$F_{\text{kin}} = \int \left( \frac{\hbar^2}{2m} |\nabla A|^2 n - \hbar |A|^2 \vec{j} \cdot \vec{\nabla} \theta \right) \frac{d^3r}{\hbar^3}, \quad (16)$$

where  $n$  and  $\vec{j}$  are the particle number and flux densities:

$$n(r) = \langle \psi_1^\dagger(r) \psi_1(r) \rangle, \quad \vec{j}(r) = -\frac{i\hbar}{2m} \langle \psi_1^\dagger(r) \vec{\nabla} \psi_1(r) \rangle + \text{h.c.} \quad (17)$$

The first term in Eq.(16) generalizes the ordinary momentum recoil energy shift to the trapped gas problem [15]. The second term represents the Doppler shift due to possible macroscopic gas flow in the sample. To clarify this, consider  $A(r) = A_0 e^{i\vec{p}r/\hbar}$ , which would describe Doppler-sensitive excitation. Then  $F_{\text{kin}} = |A_0|^2 \int (p^2/2m - \vec{p} \cdot \vec{v}) n d^3r/\hbar^3$ , where  $\vec{v} = \vec{j}/n$  is the local velocity. The sensitivity of the frequency shift to motion within the sample, manifest in the second term in Eq.(16), makes it possible, in principle, to detect vortices in the condensed state.

To employ the sum rule, one needs to relate the integrated spectral power to  $A(r)$  and  $n(r)$ . Repeating the steps that led to Eq.(12), one obtains

$$\mathcal{I}_{\text{tot}} = \int \mathcal{I}(\omega) \frac{d\omega}{2\pi} = \int |A(r)|^2 n(r) \frac{d^3r}{\hbar^3} \quad (18)$$

Combining Eq.(18) with the sum rule Eq.(12), one obtains an exact expression for the spectrum's "center of mass"  $\bar{\omega} = \int \omega \mathcal{I}(\omega) d\omega / \int \mathcal{I}(\omega) d\omega$ .

For example, consider a uniform density sample, and ignore the spatial variation of the laser field  $A(r)$ . Eq. (14) gives  $F_{\text{int}} = (\lambda_{12} - \lambda_{11}) g_2 n^2 \int |A(r)|^2 d^3r/\hbar^3$ . In our experiment  $F_{\text{kin}}$  can be neglected. Simplifying Eq.(18) and combining it with Eq.(14) yields the frequency shift Eq.(1).

There are two comments concerning the generality of the sum rule. First, note that in deriving the sum rule Eq.(12), we do not assume thermodynamic equilibrium. The result is exact and applies to non-equilibrium systems for which the factor  $g_2$  may differ from its equilibrium value. Second, the above derivation of the sum rule assumes coherence of the excitation described by (4). One can see, however, that the results (14),(16),(18) hold as well for an incoherent excitation field of the form  $A(r)e^{i\omega t + i\phi(t)}$  with a fluctuating phase  $\phi(t)$ . Also, it is

straightforward to generalize the results for the excitation field with different spatial dependence of different frequency components.

**Analysis of the data:** To investigate the utility of the sum rule, we applied it to extract a value for  $a_{1S-2S}$  from data on the  $1S-2S$  transition in hydrogen for a normal gas. An account of the experimental situation and examples of the spectral data will be published elsewhere [16]. Evaluating the integrals in the sum rule requires knowing the excitation field  $A(r)$ , the value of  $g_2$ , and the density  $n(r)$ . The excitation field is generated by a Gaussian beam which is fully characterized by a single parameter, the beam radius, which can be accurately determined. For temperatures above  $T_{\text{BEC}}$ ,  $g_2 = 2$ . At lower temperatures,  $g_2$  depends on the temperature.

The density  $n(r)$  was found by measuring the peak density and knowing the properties of the trap. The peak density  $n_0$  was determined by exploiting the property that the BEC critical density is accurately described by the ideal gas expression:  $n_c = 2.612(2\pi\hbar^2/k_B T m)^{3/2}$ . If the system is at the transition point then measuring the temperature determines the density. The system was cooled into the condensate regime and the spectrum was observed as the condensate decayed. The spectrum was measured after the condensate had decayed for ten seconds, when the presence of a small though visible condensate assured that the peak density  $n_0$  had its critical value. The contribution of the condensate to the spectrum was unimportant. Thus, the only quantity required to apply the sum rule was the temperature. This was found by measuring the width of the Doppler-sensitive spectrum [17].

From the experimentally measured spectrum we found  $\bar{\nu} = -29 \pm (2)$  KHz. We numerically calculated the integrals on the right hand side of Eqs.(14),(18) and found that  $2(\lambda_{12} - \lambda_{11})/h = 4.4 \pm (1.7) \times 10^{-10}$  Hz cm<sup>3</sup>, where the major sources of uncertainty are the temperature and the trap and laser geometry. From this we determined the  $1S-2S$  scattering length to be  $a_{12} = -1.6 \pm (0.7)$  nm. This result is in reasonable agreement with the calculated value [18],  $a_{12} = -2.3$  nm.

An alternative approach to extracting the scattering length was used in Ref. [5], where the value  $a_{12} = -1.4 \pm (0.3)$  nm was reported. The interpretation employed a semiclassical description of the atomic motion and a local density description of the phase shift. The present method is more direct and, we believe, more reliable. It can be viewed as a check on the earlier analysis, and a confirmation of the calculation of the dipolar decay constant [20] on which it depends.

In reference [10], an internally consistent description of the density of the condensate required assuming that the density shift parameter in the condensate was the same as in the normal gas, rather than half as large as expected from this analysis. This anomaly remains to be explained.

As a speculative explanation, one could consider a state close to the transition temperature in dynamical but not in thermal equilibrium, in which several low energy states are populated with macroscopic occupation numbers. For example, for  $N$  particles distributed equally among  $m$  states, one has  $n_i = N/m$ ,  $i = 1, \dots, m$  in Eq.(8). Then from Eq.(9)  $\hbar\Delta\omega_{\text{coll}} = (2 - 1/m)\lambda_{12}n$ , *i.e.*, the shift is described by an effective  $g_2 = 2 - 1/m$ . For a large number  $m$  of constituent states, the effective  $g_2$  can be arbitrarily close to 2.

In summary, we have shown that quantum statistical correlations of a cold gas sample are imprinted in the collisional shift of the center of mass of an optical absorption spectrum. In the cold collision regime the sum rule Eq.(12) can be applied to determine the statistical correlation factor  $g_2$  from optical spectrum. The sum rule is valid for any gas in the cold collision regime. It takes into account possible inhomogeneities in the sample and the excitation field, and it is valid above and below  $T_{\text{BEC}}$ . Also, the sum rule is valid for a non-equilibrium system, with  $g_2$  values possibly different from those in equilibrium. We have demonstrated the usefulness of the sum rule by using it to extract the  $1S - 2S$  scattering length for hydrogen from experimental data.

It should be pointed out that our results, the frequency shift (1) and the sum rule (12), are only valid at small mixing angles of the  $1S$  and  $2S$  states. The cold collision shift at large angle mixing is an important problem, particularly for atomic clocks. The generalization of the results (12) and (1) for such systems is an interesting open problem.

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- [4] S.J.J.M.F. Kokkelmans, B. J. Verhaar, K. Gibble, and D. J. Heinzen, Phys. Rev. A. **56**, R4389 (1997)  
B. J. Verhaar, J. M. V. A. Koelman, H. T. C. Stoof, O. J. Luiten, Phys.Rev.**A35**, 3825 (1987)  
E. Tiesinga, B. J. Verhaar, H. T. C. Stoof, D. van Bragt, Phys.Rev.**A45**, 2671 (1992)
- [5] T. C. Killian, D. G. Fried, L. Willmann, D. Landhuis, S. C. Moss, D. Kleppner, and T. J. Greytak, Phys. Rev. Lett. **81**, 3807 (1998)
- [6] W. Ketterle and H.-J. Meisner, Phys. Rev. A **56**, 3291 (1997)  
M. Naraschewski and R. J. Glauber, Phys. Rev. A. **59**, 4595 (1999)
- [7] L. D. Landau and E. M. Lifshitz, Statistical Physics I, Ch.12, §117 (Butterworth Heinemann, 1997)
- [8] C. Cesar and D. Kleppner, Phys. Rev. A. **59**, 4564 (1999)
- [9] M. Ö. Oktel and L. S. Levitov, Phys. Rev. Lett. **83**, 6 (1999)
- [10] D. G. Fried, T. C. Killian, L. Willmann, D. Landhuis, S. C. Moss, D. Kleppner, and T. J. Greytak, Phys. Rev. Lett. **81**, 3811 (1998)
- [11] T. C. Killian, Ph. D. Thesis, M.I.T, 1999 (unpublished)
- [12] S. Stringari, Phys. Rev. B. **46**, 2974 (1992)
- [13] K. Huang, *Statistical Mechanics* (John Wiley, New York, 1987), Chap. 10
- [14] M. J. Jamieson, A. Dalgarno, and M. Kimura, Phys. Rev.A. **51**, 2626 (1995)
- [15] C. L. Cesar and D. Kleppner, Phys. Rev. A **59**, 4564 (1999)
- [16] L. Willmann, D. Landhuis, S.C. Moss, T.C. Killian, D.G. Fried, T.J. Greytak, and D. Kleppner, in preparation
- [17] D. G. Fried, Ph. D. Thesis, M.I.T, 1999 (unpublished)
- [18] M. J. Jamieson, A. Dalgarno, J. M. Doyle, Mol.Phys.**87**, 817 (1996)
- [19] T. W. Hijmans, Yu. Kagan, G. V. Shlyapnikov, and J. T. M. Walraven, Phys. Rev. A **48**, 12886 (1993).
- [20] H. T. C. Stoof, J. M. V. A. Koelman and B. J. Verhaar, Phys. Rev. B **38**, 4688 (1988)

- 
- [1] A. A. Michelson, Philos. Mag. **34**, 280 (1892)
  - [2] S. Ghezali, P. Laurent, S.N. Lea and A. Clairon, Europhysics Lett. **36**, 25 (1996)  
K. Gibble and S. Chu, Phys. Rev. Lett. **70**, 1771 (1993)  
N. Allard and J. Kielkopf, Rev. Mod. Phys. **54**, 1103 (1982)
  - [3] J. Weiner, V. S. Bagnato, S. Zilio and P. S. Julienne, Rev. Mod. Phys. **71**, 1 (1999)  
P. S. Julienne, F. H. Mies, J.Opt.Soc.Am.**B6**, 2257 (1989)